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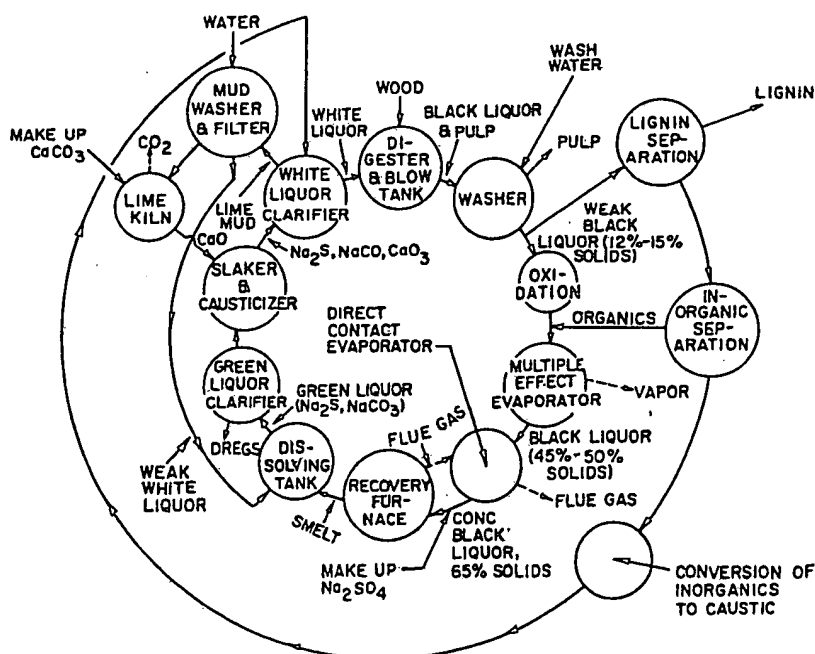
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(54) Title: KRAFT CHEMICAL RECOVERY PROCESS**(57) Abstract**

A process for increasing the pulp producing capacity of a kraft mill including the steps of removing at least a portion of the lignin from kraft black liquor and separating the lignin from the aqueous phase. The next step is treating the aqueous phase to separate the inorganics and organics with the organics preferably being recycled to the process loop to be burned in the recovery furnace. The inorganics are converted into pulping chemicals which bypass the recovery furnace and are transported to white liquor preparation.

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KRAFT CHEMICAL RECOVERY PROCESS

1 At the present time the kraft pulping process
contains a kraft recovery furnace which converts
concentrated kraft black liquor into an inorganic ash
which is then further chemically processed into caustic
5 chemicals which are used to convert wood into pulp.
Basically the kraft pulping process is a closed loop
pulping process wherein the spent kraft liquor is used to
produce the pulping chemicals that are used in the
process. However, the kraft recovery furnace is usually
10 the single most expensive piece of equipment at a kraft
pulp mill. The cost of just one kraft recovery furnace
is usually in excess of 100 million dollars. The
capacity of a kraft recovery furnace limits the total
pulp production of the kraft pulp mill. Even though the
15 rest of the kraft pulp mill could produce more pulp it is
the capacity of the kraft recovery furnace that
determines how much pulp is produced. In some cases
efforts are made that overload the recovery furnace;
however, this occurs for only short periods of time and
20 also could cause serious damage to the kraft recovery
furnace thereby forcing a shutdown of the entire kraft
pulp mill. This prevents kraft pulp mills from taking
advantage of peak demands for pulp and paper which would
substantially improve profits and return on investment.
25 It is not economically feasible for a kraft pulp mill to
install an additional kraft recovery furnace just to have
excess capacity for peak demands because of the huge
capital investment required. This approach would
dramatically reduce profits and the return on investment.
30 The present invention discloses a new process
that allows a kraft pulp mill to dramatically increase
its production of pulp without overloading the kraft
recovery furnace. In fact no additional kraft recovery
furnace is required and therefore no new investment for a
35 kraft recovery furnace is needed. This new process

1 enables a kraft pulp mill to take advantage of peak
demands for pulp and paper without the risk of
overloading the recovery furnace. In addition, this new
process provides the kraft pulp mill with additional
5 revenue from by-products that were previously burned for
their fuel value. This new process is able to accomplish
this without interfering with the chemistry of the kraft
pulp process. That is, no new chemicals or process
chemistry is introduced into the kraft pulping process.
10 This approach avoids any major investment that would be
required to make such changes.

Figure 1 illustrates the conventional process
flow diagram for the kraft pulping process. This is
still the standard process for operating kraft pulp
15 mills. In this diagram, it should be noted that the
entire process stream, the concentrated kraft black
liquor, is processed in the kraft recovery furnace to
produce an inorganic ash which is further chemically
processed into pulping chemicals.

20 The new process of the present invention (Fig.
2) may be considered basically a by-pass process wherein
after the pulp has been removed a certain percentage of
weak black liquor is removed from the process stream.
The kraft lignin that is present in the kraft black
25 liquor is removed from the process stream so that all
that remains in the kraft black liquor are the wood
sugars and other organics, organic acids and also the
inorganic or organic anion from the acid that is used to
acidify the kraft black liquor in order to remove the
30 kraft lignin.

Once the kraft lignin has been removed, the
residual liquor will contain sodium sulfate where
sulfuric acid has been used to acidify the black liquor
in order to remove the kraft lignin. Depending on the
35 size of the kraft pulp mill, this sodium sulfate may be
left in this residual liquor and concentrated and then
burned in the kraft recovery furnace. This is because

1 sodium sulfate is reduced in the recovery furnace to
produce sodium sulfide which is one of the pulping
chemicals. There is always a certain amount of sodium
sulfate added to the kraft recovery furnace in order to
5 maintain a sodium sulfide balance. Therefore the
presence of a certain amount of sodium sulfate in this
residual liquor may be tolerated with no problems.
However, once the maximum amount of sodium sulfate has
been reached it becomes necessary to remove the sodium
10 sulfate from the residual kraft liquor stream by various
means. The simplest method is to concentrate the
residual stream and then allow the sodium sulfate to
crystallize and then physically separate the sodium
sulfate crystals. The rest of the filtrate is
15 concentrated and then burned in the kraft recovery
furnace. At this point the separated sodium sulfate
crystals may be sold as an item of commerce. Under these
circumstances, other sodium compounds would have to be
added later in the process stream in order to maintain
20 the sodium balance of the system. However, it is one of
the major advantages of this invention to convert this
excess sodium sulfate into a caustic pulping chemical
such as sodium hydroxide or sodium carbonate. Not only
does this approach bypass the recovery furnace but also
25 several other steps in the processing of the ash from the
recovery furnace.

This concept is shown in Figure 2, the Bypass
Process. The economic advantages of this Bypass Process
as shown in Figure 2 will be appreciated by those skilled
30 in the art. This invention allows the kraft black liquor
to be converted to pulping chemicals by bypassing the
recovery furnace. This is accomplished by a series of
well known and established chemical reactions. One such
reaction is where the sodium sulfate is reacted with
35 calcium oxide to produce sodium hydroxide and calcium
sulfate which is insoluble. The sodium hydroxide is a
pulp chemical and calcium sulfate which is gypsum can

1 be used as pigment or sold into commerce as a commodity
chemical.

Figure 2 showing the invention illustrates the
lignin separation from the weak black liquor which passes
5 to an inorganic separation. Organics from this step are
channeled to the recovery furnace and inorganics go to a
conversion station where conversion to caustic takes
place. This material is then used in producing white
liquor.

10 The choice of acid that is used to precipitate
the kraft lignin may depend on the commercial value of
the calcium anion. For instance if phosphoric acid is
used, then calcium phosphate is produced which will
separate and can be sold as a commercial fertilizer. If
15 carbon dioxide is used, then sodium carbonate is produced
which may be reacted with calcium oxide to produce sodium
hydroxide, a pulping chemical.

The following examples illustrate the teachings
of the present invention.

20 In the following examples, the exact amount of
sodium in kraft black liquor will vary depending on the
source of the kraft black liquor. In these examples, the
principle is being demonstrated.

25

EXAMPLE I

The kraft lignin is removed by using various
techniques (such as disclosed in U.S. Patent No.
4,111,928) from 3,000 parts of weak kraft black liquor
(approximately 15% solids). Sulfuric acid is used to
30 acidify the kraft black liquor and the residual solution
contains sodium sulfate. At this point, it is necessary
to remove the sodium sulfate because it is necessary to
maintain the proper sodium and sulfur balance in the
system. The residual solution is concentrated to 50-60%
35 solids and then this solution is allowed to cool to room
temperature and the sodium sulfate readily crystallizes

1 out and is easily separated from the solution by
filtration or other appropriate method.

Once the sodium sulfate crystals are removed,
the residual solution may be burned in the recovery
5 furnace to recover the heat value of the organics that
are present. One should note that the first
crystallization may not remove all of the sodium sulfate.
However, the amount of sodium sulfate that remains in
solution may be tolerated by the system since most kraft
10 pulp mills do add a certain amount of sodium sulfate
directly to kraft recovery furnaces in order to maintain
the sulfur balance in the system. The separated sodium
sulfate may be sold to outside customers.

15 EXAMPLE II

The kraft lignin is removed by using various
techniques (as above noted) from 3,000 parts of weak
kraft black liquor (approximately 15% solids). Sulfuric
acid is used to acidify the kraft black liquor and the
20 residual solution contains sodium sulfate. At this
point, it is necessary to remove the sodium sulfate
because it is necessary to maintain the proper sodium and
sulfur balance in the system. The residual solution is
concentrated to 50-60% solids and then allowed to cool to
25 room temperature and the sodium sulfate readily
crystallizes out and is easily separated from the
solution by filtration or some other appropriate method.

Once the sodium sulfate crystals are removed,
the residual solution may be burned in the recovery
30 furnace to recover the heat value of the organics that
are present. One should note that the first
crystallization may not remove all of the sodium sulfate.
However, the amount of sodium sulfate that remains in
solution may be tolerated by the system since most kraft
35 pulp mills do add a certain amount of sodium sulfate
directly to kraft recovery furnaces in order to maintain
the sulfur balance in the system.

1 However, in order to utilize the sodium sulfate
so that the sodium balance is maintained without adding
outside sodium, the sodium sulfate may be converted to a
caustic pulping chemical. Here 215 parts of sodium
5 sulfate (anhydrous weight) are dissolved in 800 parts of
water and then 84 parts of calcium oxide is added under
agitation and the temperature of this mixture is heated
to 180 F. for two hours or until the sodium sulfate is
mostly converted into sodium hydroxide and the calcium
10 oxide is precipitated as calcium sulfate. The calcium
sulfate is filtered or separated by other means, and
solution that is left is a caustic solution that can be
used for pulping. The separated calcium sulfate is a
form of gypsum and may be used as a pigment for some
15 paper coatings or sold to outside markets.

EXAMPLE III

 In this example, phosphoric acid is to acidify
the kraft black liquor. The kraft lignin is removed by
20 various techniques (as above noted) from 3,000 parts of
weak black liquor (approximately 15% solids). Since
phosphoric acid is used to acidify the kraft black
liquor, then the residual solution will contain sodium
phosphate. At this point, it becomes necessary to remove
25 the sodium phosphate because it is necessary to keep the
phosphate ion out of the system.

 Then the residual solution is concentrated to
50 to 60% solids and at room temperature the sodium
phosphate will readily crystallize out and is easily
30 separated from the solution by filtration or some other
appropriate method. Once the sodium phosphate is
removed, then the residual solution may be burned in the
recovery furnace to recover the heat value of the
organics that are present. The separated sodium
35 phosphate may be sold to outside customers.

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EXAMPLE IV

In this example, phosphoric acid is to acidify the kraft black liquor. The kraft lignin is removed by various techniques (as noted above) from 3,000 parts of weak black liquor (approximately 15% solids). Since phosphoric acid has been used to acidify the kraft black liquor the residual solution will contain sodium phosphate. At this point, it becomes necessary to remove the sodium phosphate because it is necessary to keep the phosphate ion out of the system.

Then the residual solution is concentrated to 50 to 60% solids and at room temperature the sodium phosphate will readily crystallize out and can be easily separated from the solution by filtration or some other appropriate method. Once the sodium phosphate is removed, then the residual solution may be burned in the recovery furnace to recover the heat value of the organics that are present.

The separate sodium phosphate may be converted to calcium phosphate which is a valuable fertilizer. This is accomplished by concentrating the residual solution and allowing the sodium phosphate to crystallize out. This crystallized sodium phosphate (approximately 200 parts anhydrous), can be separated and then dissolved in 1,000 parts of water. Then 252 parts of calcium oxide is added under agitation and the temperature of this mixture is heated to 180 F for two hours or until the sodium phosphate is converted into sodium hydroxide and the calcium oxide is precipitated as calcium phosphate. The calcium phosphate may be filtered or separated by other means and the solution that is left is a caustic solution that may be used for pulping. The separate calcium phosphate can be sold as a fertilizer or to other markets.

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EXAMPLE V

In this example, the kraft lignin is

1 insolublized by using carbon dioxide gas.

Kraft lignin is removed by various techniques (as noted above) from 3,000 parts of weak black liquor (approximately 15% solids) after the carbon dioxide gas
5 has been allowed to insolublize the kraft lignin by various techniques. At this point, the residual solution may be concentrated and burned in the kraft recovery furnace, or the residual solution could be concentrated to at least 50% solids so that the sodium carbonate or
10 sodium bicarbonate will crystallize out and therefore be easily filtered or separated from the solution by various techniques.

Then 40 parts of sodium carbonate (anhydrous weight) is added to 500 parts of water in a suitable
15 container. Then 22.4 parts of calcium oxide is added under agitation and the temperature of this mixture is heated to 180 F. for two hours or until the sodium carbonate is converted into sodium hydroxide and the calcium oxide is precipitated out as calcium carbonate.

20 In an actual kraft pulp mill, the sodium carbonate may be sent to a slacker and causticizer where this sodium carbonate will be converted into sodium hydroxide.

Under atmospheric pressure, carbon dioxide gas
25 will not insolublize all of the lignin that is present in kraft black liquor. However, it is not necessary to remove all of the kraft lignin from the kraft black liquor. Sodium carbonate or sodium bicarbonate that is formed actually need not be removed from the solution
30 since the recovery furnace is capable of processing these materials. However, since it is the intent of this invention to bypass the recovery furnace, the sodium carbonate and sodium bicarbonate may be removed prior to the recovery furnace and then added to the slacker and
35 causticizer.

These are one of the major advantages of this

1 new invention. It allows different materials to be used
to derive the maximum value for its products and
by-products. This new invention allows a kraft pulp mill
to increase its production of pulp by as much as 20% or
5 even higher without the huge capital investment for a
recovery furnace.

This invention has been described in detail
with particular emphasis on the preferred embodiments
thereof, but it should be understood that variations and
modifications within the spirit and scope of the
10 invention may occur to those skilled in the art to which
the invention pertains.

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1 What is claimed is:

1. A process for use in the kraft pulping process which uses a recovery furnace and a wood digester including treating kraft black liquor from the wood digester to render all or part of the kraft lignin insoluble in the aqueous phase, removing the insoluble kraft lignin from the aqueous phase, processing the aqueous phase to separate inorganic chemicals contained therein, converting the inorganic chemicals into pulping chemicals and transporting the pulping chemicals to the digester to digest wood products and without passing them through the recovery furnace.

2. A process as in Claim 1 wherein the kraft black liquor from the wood digester is acidified to render the lignin insoluble in the aqueous phase.

3. A process as in Claim 2 wherein said acidification is accomplished by the use of sulfuric acid.

4. A process as in Claim 2 wherein said acidification is accomplished by the use of phosphoric acid.

5. A process as in Claim 2 wherein said acidification is accomplished by the use of carbon dioxide.

6. A process as in Claim 3 wherein the inorganic material that is separated is sodium sulfate.

7. A process as in Claim 3 wherein the sodium sulfate is reacted with calcium oxide or calcium hydroxide to produce sodium hydroxide.

8. A process as in Claim 5 wherein the inorganic material that is separated is sodium bicarbonate.

9. A process as in Claim 8 wherein the sodium bicarbonate is converted into sodium carbonate.

10. A process as in Claim 3 wherein the sodium sulfate is reacted with barium oxide or barium hydroxide to produce sodium hydroxide.

1 11. A process as in Claim 2 wherein said
acidification is accomplished by the use of sulfur
dioxide.

5 12. A process as in Claim 4 wherein sodium
phosphate is reacted with calcium oxide or calcium
hydroxide to produce sodium phosphate.

10 13. A process as in Claim 1 wherein the
aqueous phase remaining after the inorganic chemicals
therein are separated is transported to the recovery
furnace to be burned.

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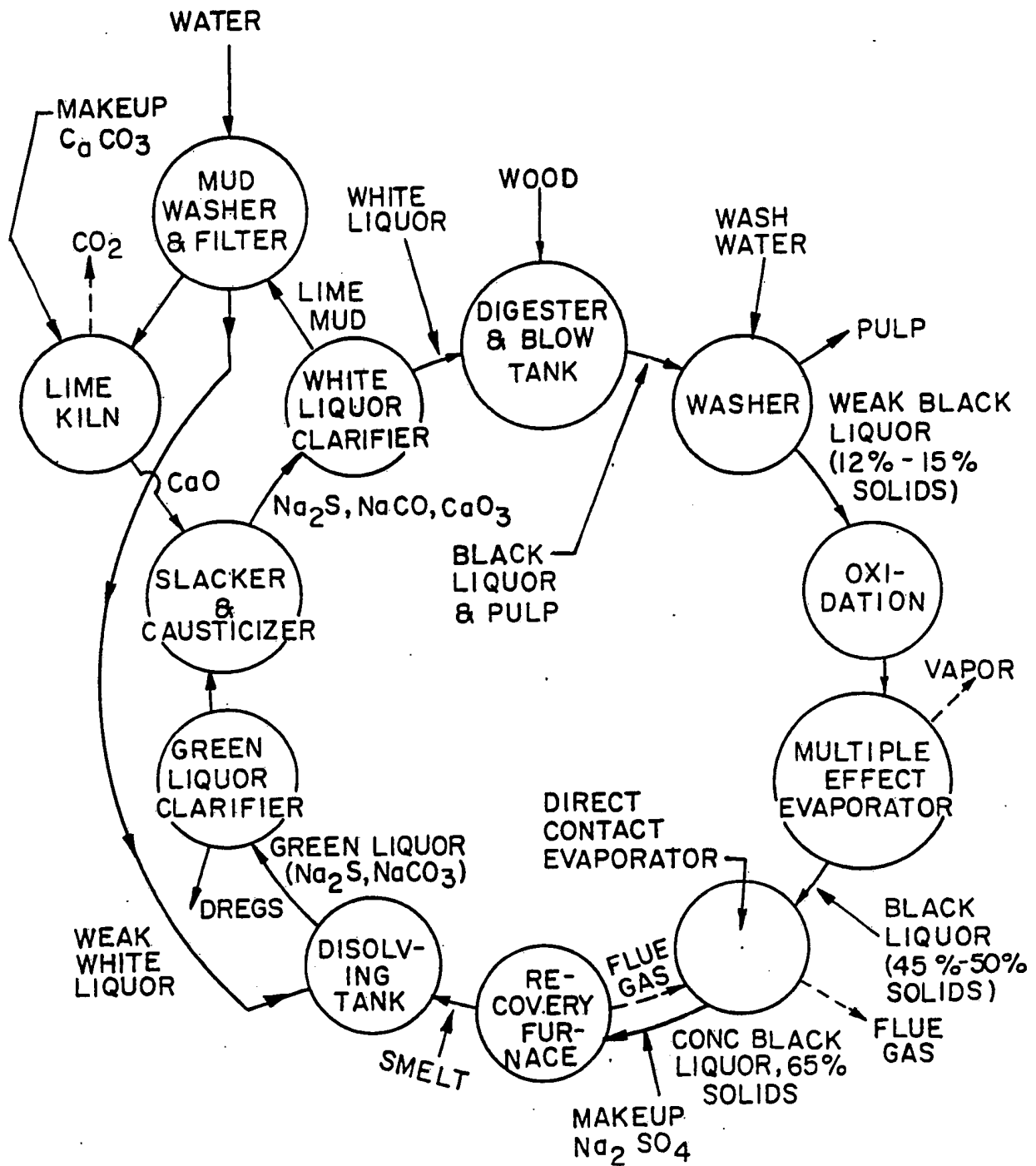
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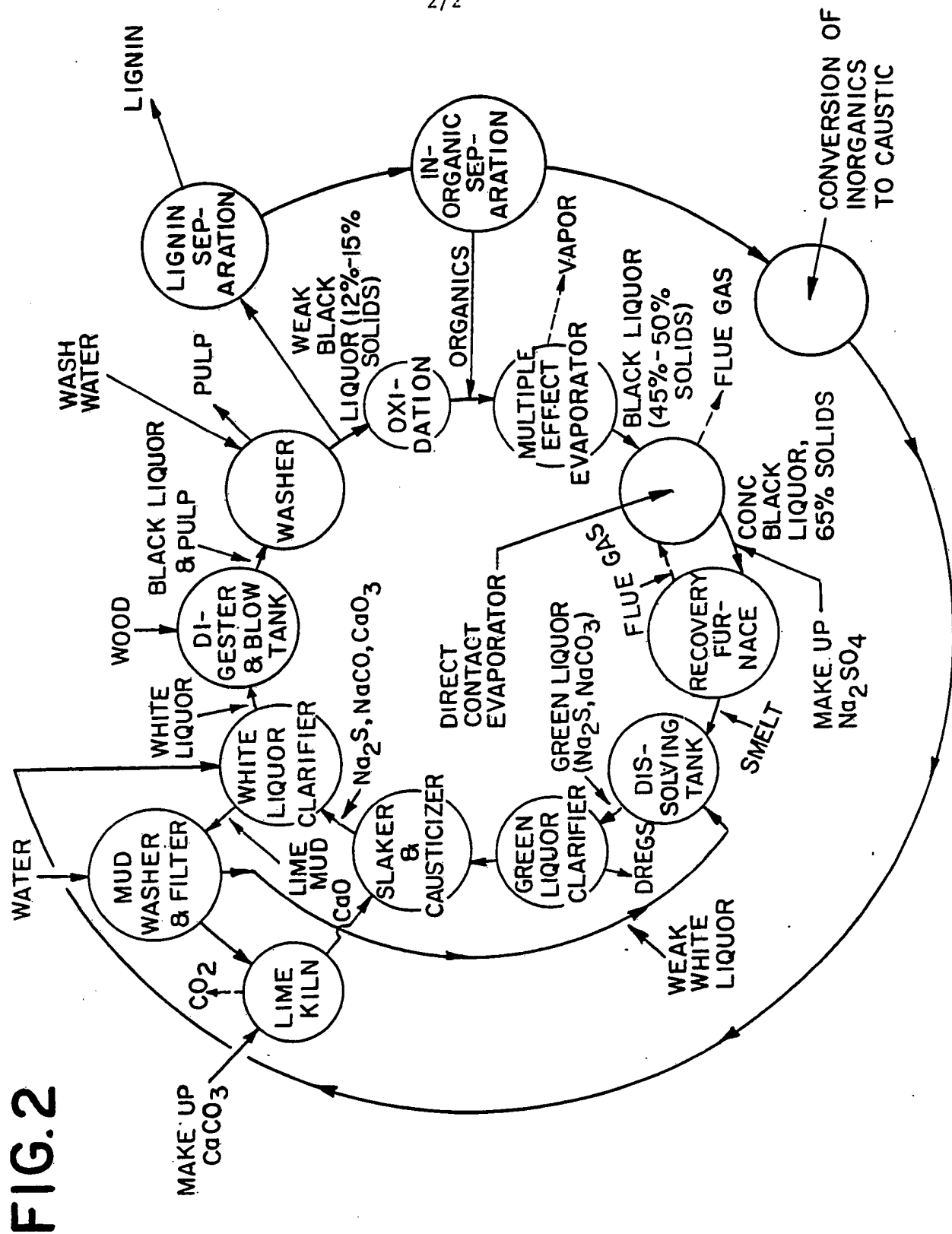
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FIG. 1

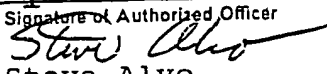


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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/03801

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC(4): D21C 3/02 11/04 U.S.CL.: 162/30.11, 38		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	162/ 16, 30.1, 30.11, 38, 80 210/928	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 4,470,876 (BEAUPRE) 11 SEPTEMBER 1984 SEE COLUMN 2, LINE 23- COLUMN 3, LINE 52 AND THE FIGURE.	1-13
Y	US, A, 4,507,172 (STELTENKAMP) 26 MARCH 1985 SEE COLUMN 4, LINES 46-51 AND FIGURE 2.	1-13
Y	SU, A, 730,914 (CELL-PAPER DES INST) 30 APRIL 1980. SEE ABSTRACT.	4, 12
A	US, A, 3,986,923 (REEVE) 19 OCTOBER 1976 SEE FIGURE 1.	
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
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ISA/US		 Steve Alvo